

Supplementary Material (ESI) for CrystEngCommunity
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Electronic Supplementary Information

Facile Synthesis of Germanium-Graphene Nanocomposites and Their Application as Anode Material for Lithium Ion Batteries

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1. Experimental

1.1 Chemicals

Germanium tetrachloride (99.999% trace metals basis) and germanium powder (100 mesh, 99.999%) were purchased from Sigma-Aldrich China Inc.. Sugarcane bagasse (SB) was obtained from Liangci Manufacturing Co. Ltd. of the Guangxi Zhuang Autonomous Region of China. Other chemicals were purchased from Beijing Chemical Reagent (Beijing, China). All solvents were of analytical grade. Other chemicals were purchased from Beijing Chemical Reagent (Beijing, China). All solvents were of analytical grade.

1.2 Instruments

Two swagelok-type cells were used in this work. The working electrode was fabricated by compressing a mixture of the active materials (Ge NPs/GR composites), conductive material (acetylene black), and binder (polytetrafluoroethylene) in a weight ratio of 78:12:10, pasted on pure copper foil, and then vacuum-dried at 383K overnight. Pure lithium foil was used as the counter electrode. The electrolyte solution was prepared by dissolving 1 M LiPF₆ in a solution of ethylene carbonate (EC), dimethyl carbonate (DMC), and diethyl carbonate (DEC) (EC:DMC:DEC 1:1:1, v/v/v). The cells were assembled in an argon-filled Labconco glove box. Discharge/charge curves and capacity cycle performance were tested at different current densities in the voltage range of 0.01-3 V on a Land CT2001A test system. Electrochemical impedance measurements were carried out on a PARSTAT 2273 potentiostat/galvanostat. The Nyquist plots were recorded by applying an AC voltage of 5 mV amplitude in the frequency range of 100 kHz to 100 mHz.

The powder X-ray diffraction (XRD) measurements of the samples were recorded on a Bruker D8- Advance X-ray powder diffractometer using Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) with scattering angles (2θ) of 10–70°. JEOL JEM 1200 EX and JEOL JEM 2010 transmission electronic microscopy were used for transmission electron microscopy (TEM) analysis and high-resolution transmission electron microscopy (HRTEM), respectively. The JEOL JEM 2010 instrument is equipped with energy dispersive X-ray spectroscopy (EDS, Oxford) and selected area electron diffraction (SAED) analysis at an accelerating voltage of 100 kV. Samples were prepared by placing one drop of an ethanol suspension of the Ge NPs/graphene hybrid

composites onto a copper grid (3 mm, 200 mesh) coated with carbon film. Thermogravimetric analysis (TGA) was carried out on a TA instrument TGA-2050 after calcining the materials at 800 °C in air.

1.3 Synthesis of Ge NPs/GR Nanocomposites and GR

SB was activated by physical activation, which involved below steps: ¹⁻² 1) carbonization process of SB by using of a dehydrating agent, sulfuric acid, followed by 2) gasification with carbon dioxide at 900 °C. 3) In the carbonization step, concentrated H₂SO₄ was added to SB in an optimum ratio of 3 : 4 (weight ratio). The blend was packed into a Pyrex reactor and heated to 160 °C for two hours with air. Air was metered into the reactor at the rate of 120 dm³/s. The resulting carbon was cooled and washed with water until acid free and then dried at 110 °C. GO was prepared by modified Hummers method starting from SB derived graphite ³⁻⁶. In a typical synthesis, the obtained GO (250 mg) and GeCl₄ (0.3 mL) were suspended in DMF (double distilled), the mixture was then sonicated for 45 minutes. Under these situations, the oxygen-containing groups in GO structure could provide plentiful joining sites for anchoring precursor Ge (IV) ions and make them enrich in some places. In the second step, excessive sodium powder (700 mg) was added slowly to the above mixture under stirring. The mixture was then sonicated for another 5 minutes and stirred for 24 hours under room temperature, the GO and Ge (IV) ions were reduced *in situ* and resulted into Ge NPs loading on GR nanosheets. Finally, the solid sample was collected after thorough washing with ethanol and deionized water

to remove unanchored Ge (IV) ions. The sample was vacuum-dried at 60 °C for 24 hours and afforded the Ge NPs/GR composites.

Similarly, GR was prepared by simply reduction of GO (250 mg, 1 mg/ml, in DMF) with sodium powder (700 mg), the obtained product was washed thoroughly with ethanol and deionized water. After vacuum-dried for 24 hours, GR was obtained readily.

2. Figures

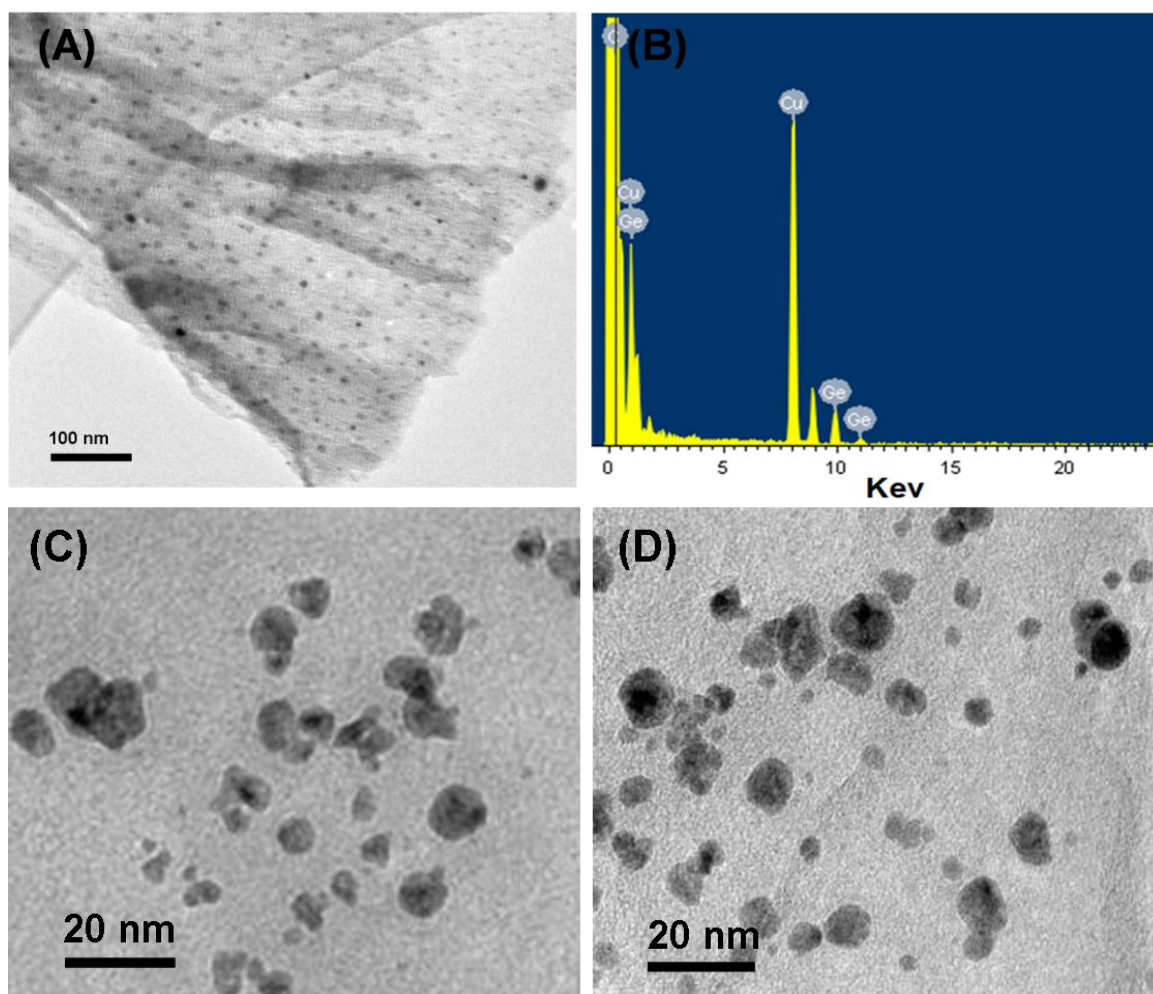


Figure S1. TEM image of Ge NPs/GR (A) and EDS analysis of Ge NPs/GR (B);
TEM images of Ge NPs/GR after charge (C) and discharge (D).

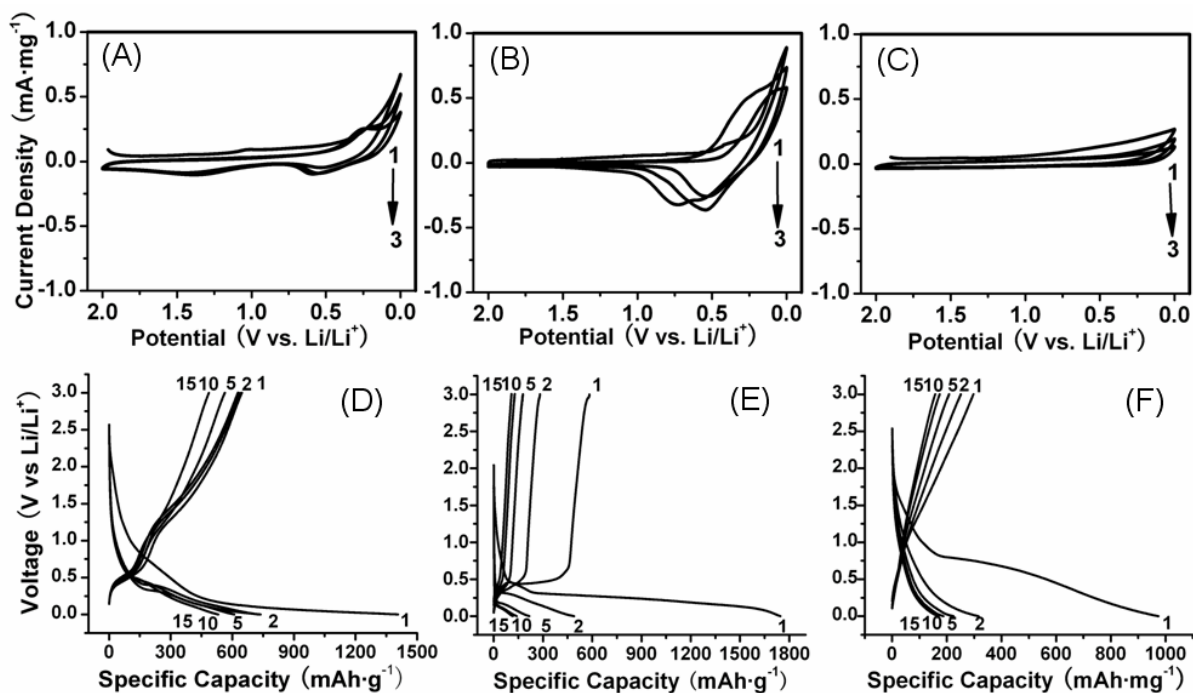


Figure S2. CV curves for the first three cycles of Ge NPs/GR (A), Ge (B) and GR (C), Scan rate: 0.1 mV·s⁻¹; Voltage-capacity profiles for the 1st, 2nd, 5th, 10th and 15th cycles of Ge NPs/GR (D), Ge (E) and GR (F), current rate: 200 mA·g⁻¹.

References

1. M. Ruiz, C. Rolz. *Ind. Eng. Chem. Prod. Res. Dev.* **1971**, *10* (4), 429–432.
2. B. S. Girgis, L. B. Khalil, T. A. M. Tawfik. *J. Chem. Technol. Biotech.* **1994**, *61*, 87–92.
3. Y. M. Li, L. H. Tang, J. H. Li. *Electrochem. Commun.* **2009**, *11* (4), 846–849.
4. H. L. Wang, J. T. Robinson, G. Diankov, H. J. Dai. *J. Am. Chem. Soc.* **2009**, *131*, 15939–15944.
5. W. S. Hummers, R. E. Offeman. *J. Am. Chem. Soc.* **1958**, *80*, 1339–1139.
6. Y. Wang, Z. H. Li, D. H. Hu, C.-T. Lin, J. H. Li, Y. H. Lin. *J. Am. Chem. Soc.* **2010**, *132*, 9274–9276.